ELECTRICAL PROPERTIES STUDY OF SILVER NIOBATE($AgNbO_3$)AND ITS MODIFIED SYSTEM($AgNb_{1-x}M_xO_3$)where M=Ta(Tantalum),Sb(Antimony),V(Vanadium)

Annual Project Report

2014-2015

Thesis on partial fulfillment of degree in M.Sc.(Physics)

Submitted by:

Sanjay Kumar

413 PH 2085

M.Sc. Physics

Department (Physics & Astronomy)

Under the guidance of

Prof. S. Panigrahi

NATIONAL INSTITUTE OF TECHNOLOGY ROURKELA

DEPARTMENT OF PHYSICS AND ASTRONOMY

CERTIFICATE

This is to certify that SANJAY KUMAR has carried out and successfully completed the annual project entitled "Electrical properties study of silver niobate($AgNbO_3$) and its modified system ($AgNb_{1-x}M_xO_3$) where M=Tantalum,Antimony,Vanadium" at NIT Rourkela.

This is an authentic work carried out by him under my supervision and guidance in Thin film laboratory of the Department of Physics & Astronomy.

Prof. S. Panigrahi

Dept. of Physics

NIT Rourkela

ACKNOWLEDGEMENT

I would like to thank Prof.Simanchala Panigrahi for his valuable guidance and constant supervision as well as providing necessary information regarding the project. I amgreatful to PhD scholars Mr. Rakesh Muduli, Mr. Ranjit Panda, Mr. Ranjit pattanayak, Mrs. Priyambada Nayak for their valuable suggestions and clarifying all my doubts. I would like to acknowledge my deep sense of gratitude to Prof. DhrubanandaBehera and Prof.Pawan Kumar for allowing me to use the facilities in theirlaboratory.

I also express my especially thankfulness to PhD scholar Rakesh Muduli for helping me in completing my project and analyzing the data.

NIT Rourkela

April 2015

Sanjay Kumar

413 PH 2085

M.Sc. Physics(2 yr.)

Contents

List of figures:

Abstract:

The fundamental study on effect of isovalent cationic substitution on the electric properties of silver niobate ($AgNbO_3$) which shows week hysteresis loop of polarization vs electric field. The modification were carried out in place of pentavalent Nb (B-site of ABO_3 perovskite structure) by Ta^{5+},Sb^{5+},V^{5+}.We followed the mixed oxide route to syenthesize the compound $AgNb_{0.9}M_{0.1}O_3$($M=Ta^{5+}$,Sb^{5+}, and V^{5+}).The formation of desired phases was confirmed by XRD technique and surface morphologies of prepared sample were photographed by FESEM. Dielectric, ferroelectric and electric transport properties were investigated. Enhanced dielectric and ferroelectric values were observed in the modified system and this enhancement is found more in Sb modified system. The relaxation behavior of conducting dipoles was analysed by complex impedence technique. It is found that only intrinsic relaxation (grain) exists in the parent as well as in the modified system.

CHAPTER 1

Introduction of dielectric material

A dielectric material is an electric insulator that can be polerised by an external electric field.When we placed a dielectric material in an electric field electric charge do not flow through the material(because it is an insulator) but only slightly shift from their average equilibrium position cause electric polerisation.All dielectric material are made up of insulator so all dielectric are insulator but all insulator are not dielectric.

Because of dielectric polerisation positive charge are displaced toward field and negative charge in the opposite direction in **fig (1)**This create an internal electric field which reduce the overall field in the dielectric itself.

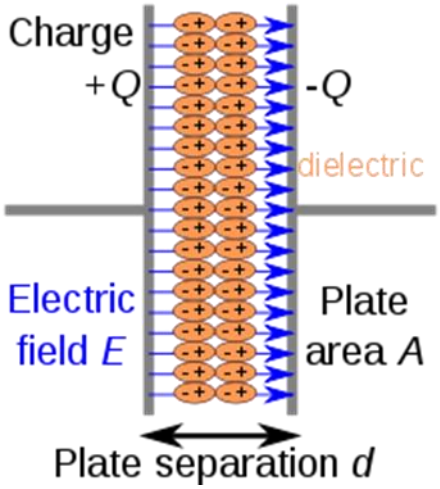
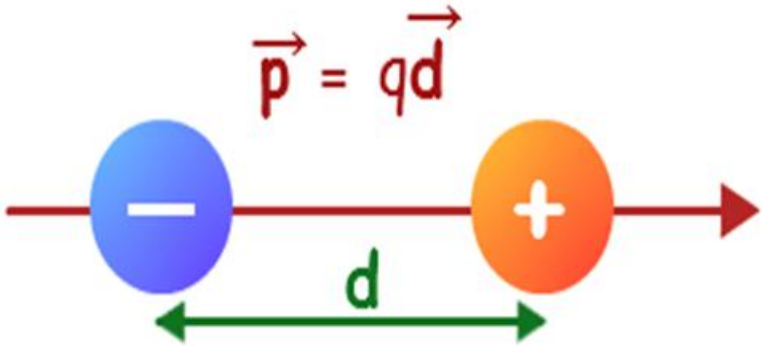


Fig 1

Fig 2



When dielectric material are polerised so we can say that there is polar character and due to polar character arise electric dipole moment and mathematicaly we can define electric dipole moment is the product of magnitude of either charge and the distance of separation between them.generalyit is defined by p and p=q.d, where d is the displacement vector pointing from the negative charge to the positive charge as shown in **fig.2**

Some term related to dielectric:

1. Dielectric constant(ε_r):It is the ratio of absolute permitivity(ε)to the permittivity of free space(ε_0) and it is given by $\boldsymbol{\varepsilon_r=\varepsilon/\varepsilon_0}$

2. Electric susceptibility(χ_e):It is the dimensionless proportionality constant that indicate the degree of polerisation of a dielectric material in response to an applied electric field.The greater the electric susceptibility greater the ability of a material to polarize in response to field.Mathematicaly It is related to E and P

$$\mathbf{P=\varepsilon_0\chi_eE}$$

Where symbol has their usual meaning

3.Polerisation density(P):In classical electromagnetism it is the vector field that express the density of permanent or induced electrical dipole moment in a dielectric material.Mathematicaly

$$\mathbf{P=d/v}$$

4.Electric displacement(D):It account the effect of free and bound charge with in material and

$$\mathbf{D=\varepsilon_0E+P}$$

Dielectric polerisation and its type

Dielectric Polerisation:It is the property of a dielectric material due to which positive charge are displaced toward the electric field and negative charge shift in the opposite direction.

It has mainly four type

1.Ionicpolerisation

2.Dipolarpolerisation

3.Electricpolerisation

4.Space charge polerisation

Now we discus these one by one

1.Ionic Polerisation:It is a polerisation caused by relative displacement between positive and negative ions in ionic crystal (NaCl) and displacement is independent of tempreture.

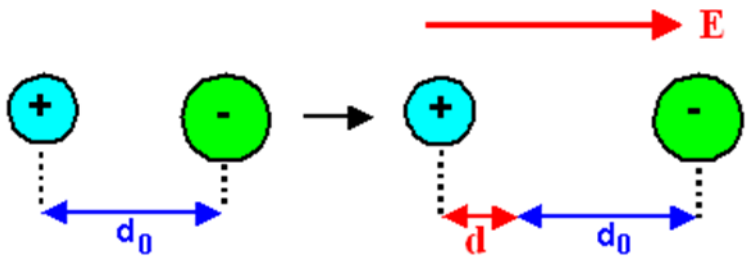


Fig.3

Dipolar polerisation:It is a polerisation that is either inherent to polar molecule (orientation polerisation) or can be induced in any molecule in which asymmetric distortion of nuclei is possible (distortion polerisation).Orientation polerisation result from a permanent dipole which retain polerisation in the absence of external electric field. Eg.H_2O

Electric polerisation:In classical electromagnetism polerisation density is the vector field that express the density of permanent or induced electric dipole moment in a dielectrc material.When a dielectric is placed in an external electric field its molecule gain electric dipole moment and the dielectric is said to be polerised.

Space charge polerisation:Space charge polerisation occur due to diffusion of ions along the field direction.

Introduction of ferroelectric material:

A ferroelectric material is a material that exhibits, over some range of tempreture,a spontaneous electric polerisation that can be reversed or reoriented by application of an electric field.A necessary criterion is the requirement of an ever present spontaneous polerisation,with the requirement of reversibility or reorientation of that spontaneous polerisation being a sufficient criterion for a ferroelectric phase.Thus ferroelectric effect is an electrical phenomenon whereby certain crystal may exhibit a spontaneous dipole moment.eg. $Pb(Zr,Ti)O_3$ (PZT), $BaTiO_3$,

Typically materials demonstrate ferroelectricity only below a certain phase transition tempreture,called the Curie tempreture and are paraelectric above this tempreture.

CHAPTER 2

Literature Review

History of ferroelectrics:

Ferroelectric ceramics were born in the early 1940s with the discovery of phenomenon of ferroelectricity as the sourace of unusually high dielectric constant in ceramic barium titanatecapacitors.Since at that time they have been the heart and soul of several multibillion industries,ranging from high dielectric constant capacitors to later development in piezoelectric transducer,positive tempreture coefficient devices,and electro optic light valve.Material based on two compositional systems barium titanate and lead zirconium titanate have dominated the field throughout their history.The most recent development in the field of ferroelectric ceramics such as medical ultra-sonic composites,photostrictors,and thin and thick film for piezoelectric and integrated circuit application have served to keep the industry young amidst its growing maturity.Various ceramic formulation their form(bulk,film),fabrication and functional properties and future is described in relation to their ferroelectric nature and specific area of application.Since the discovery of ferroelectricity in single crystal material potassium sodium tartrate(Rochelle Salt) in 1921 and its subsequent extension into the realem of polycrystalline ceramics barium titanate during the early mid 1940,there has been a continuous sucession of new material and technology development that have lead to a significant number of industrial and commerecial application that can be directly created to this most unusual phenomenon.Among these application are high dielectric constant capacitor,piezoelectric sonar and ultra sonictransducer,radio and communication filter,pyroelectric security surveillance devices,medical diagnostic transducer,stereotweeters,buzzers,gasignitors,positive tempreture coefficient sensors and switches,ultrasonicmotors,electro optic light valve,thin film capacitors and ferroelectric thin film memories.

Ferroelectric crystal

A ferroelectric crystal exhibit an electric dipole moment even in the absence of external electric field.In the ferroelectric state the center of positive charge of the crystal does not coinside with the center of negative charge.The internal electric dipole of a ferroelectric material are coupled to the material lattice so anything that change the lattice can change the strength of dipole (in other word a change in spontaneous polerisation).The change in spontaneous polerisation result in the change in surface charge.This can cause the current flow in the ferroelectric capacitor even in the absence of an external voltage across the capacitor.Two stimuli that change the lattice dimension of a material are force and tempreture.The generation of a surface charge in the response of an application of an external stress to a material is **piezoelectricity**.A change in the spontaneous polerisation of a material in response to change in tempreture is called **pyroelectricity**.

Generally there are 230 space group among which 32 crystalline class can be found in crystal.There are 21 non centrosymmetric class,with in which 20 are piezoelectric .Among the piezoelectric class 10 have spontaneous electric polerisationthat varies with the tempreture therefore they are pyroelectric.Among pyroelectric some of them are ferroelectric.

About $AgNbO_3$

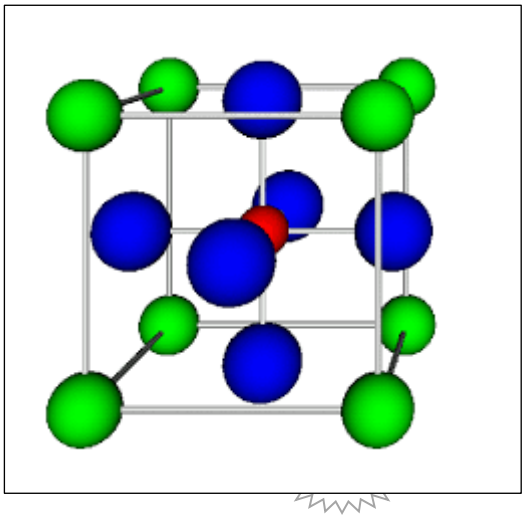
Silver niobate ($AgNbO_3$) has been reported first by Francombe and Lewis in 1958.It has many interesting properties from both the theortical and application point of view.Ferroelectricity,chargeordering,spin dependent transport,magnetic and transport properties are commonly observed.Silverniobate has perovskite structure which we will discuslater.This perovskite type $AgNbO_3$ has a good crystal phases at different tempreture and different doping.$AgNbO_3$ also shows the photocatalyticactivity.However its photocatalytic activity for decomposition of organic pollutants is not high.So metal ion or metal oxide are used to promote the photocatalytic activity.

Polerisation measurement shows that $AgNbO_3$ has an extremaly large polerisation.Experiment also shows that the large internal atom distortion in $AgNbO_3$ is strongly coupled with electric field indicating that high piezoelectric strength in $AgNbO_3$ system.

For pure phase $AgNbO_3$ X ray diffraction analysis reveals that it crystallizes in the orthorhombic perovskite lattice with a space group of $Pmc2_1$and cell parameter a=15.69 Å,b=5.55 Å, c=5.58 Å. The tempreture, pH value ,time play an crucial role in obtaining phase pure silver niobate.

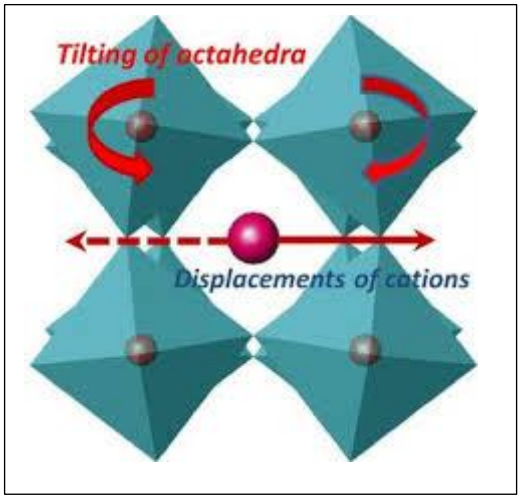
Structure of $AgNbO_3$

The structure of $AgNbO_3$ is like ABX_3or simply we can say that perovskite structure after the name of Perovski.Here A and B are two cation of different size and X is anion that bonds the both.The A atom is larger than the B atom.The perovskite structure is adopted by many oxide which has the formula ABO_3.In the idealized cubic unit cell of such a compound type A atom sit at cubic corner position (0,0,0). Type B atom sit at body center position (1/2,1/2,1/2) and oxygen atom sit at face center position(1/2,1/2,0) which is shown in **fig.4**

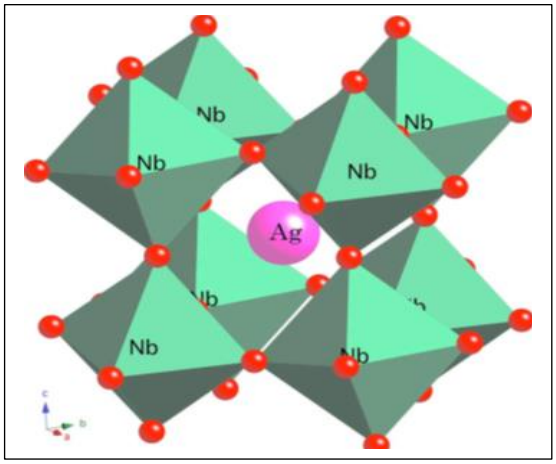


The ideal cubic-symmetry structure has the B cation in 6-fold coordination, surrounded by an octahedron of anions, and the A cation in 12-fold cuboctahedral coordination. The relative ion size requirements for stability of the cubic structure are quite stringent, so slight buckling and distortion can produce several lower-symmetry distorted versions, in which the coordination numbers of Acations, B cations or both are reduced.

Tilting of the BO_6 octahedra reduce the coordination of an undersized Acation from 12 to as low as 8 and this tilting is shown in **fig.5**



Pseudo-perovskite unit cell at room tempreture also shown in **fig.6**



CHAPTER 3

Experimental method:

Syenthesis of the material

There are several syenthesis method but I use here only two method for syenthesis

1.Sol-gel method

2.Solid state reaction method

1.Sol-gel method:It is very popular method for syentesis.Heresyenthesis of silver niobate($AgNbO_3$).It syenthesised by silver nitrate and niobium oxalate hydrate.

Silver nitrate ($AgNo_3.H_2O$) Molecular wg.=169.87 g mol^{-1}

Niobium oxalate hydrate($C_{10}H_5NbO_{20}$).xH_2O Molecular wg.=538.04 g mol^{-1}

We take always ratio of Ag and Nb 1:1.First we take 100 ml water in a beaker and then add 1:1 ratio of above powder.

169.87/100 : 538.04/100 = 1.6987 : 5.3804

Then we add Glycin($C_2H_5NO_2$) Molecular wg.=75.07 g mol^{-1}

It act as a reagent and add in the ratio 1:1:4.

75.07/100 =0.7507 ratio is 1:1:4 so 0.7507*4=3.0028g

Then we shake the solution for dissolving the compound and heat the mixture and stir with the help of magnetic stirrer until all water(solvent) vaporate and a black powder remain in the glass.We cool down the mixture in beaker and after that we take the powder for grinding 40 minutes and then calcination of chemical compound at $500^{0c}$for 3 hrs.and take the XRD data.

2.Solid state reaction method:

First syenthesis of silver niobate($AgNbO_3$) in pure form and then we confirm the phase.After doping it takes the form $Ag(Nb_{1-x}M_x)O_3$ where M=Tantalum(Ta),Antimony(Sb),Vanadium(V) etc.

Calculation

1.M=Tantalum(Ta)

Molecular wg. Of Ag_2O=231.74 g mol^{-1}

Molecular wg. Of Nb_2O_5=265.81 g mol^{-1}

Molecular wg. Of Ta_2O_5=441.893 $gmol^{-1}$

For 1 Ag atom: 231.74/2=115.87 g mol^{-1}

For 1 Nb atom: 265.81/2=132.91g mol^{-1}

For 1 Ta atom: 441.893/2=220.95g mol^{-1}

We prepare 5 g sample and first pure form($AgNbO_3$) means x=0.It can be syenthesised by silver oxide(Ag_2O) and niobium pentaoxide(Nb_2O_5)

Total amount=(115.87+132.91)=248.78 g

Ag_2O amount=115.87*5/248.78=2.3287g

Nb_2O_5 amount=132.91*5/248.78=2.6712g

X=0.1(10%)$Ag(Nb_{0.9}Ta_{0.1})O_3$

Total amount=[115.87+(0.9*132.91=119.62)+(0.1*220.95=22.095)]=257.58g

Ag_2O amount=115.87*5/257.58=2.2492+(3% extra wg.=0.03*2.2492=0.0674)=2.3166g

We take 3% extra wg because in calcination there is some volatilization means 3% in stable equilibrium after volatile process amount will be not much disturbed.

Nb_2O_5=119.62*5/257.58=2.3219g

Ta_2O_5=22.095*5/257.58=0.4289g

X=0.2(20%) $Ag(Nb_{0.8}Ta_{0.2})O_3$

Total amount=[115.87+(0.8*132.91=106.328)+(0.2*220.95=44.19)]=266.388g

Ag_2O=115.87*5/266.388=2.1748+(3% extra=0.0652)=2.2400g

Nb_2O_5=106.328*5/266.388=1.9957g

Ta_2O_5=44.19*5/266.388=0.8294g

X=0.3(30%) $Ag(Nb_{0.7}Ta_{0.3})O_3$

Total amount=[115.87+(0.7*132.91=93.037)+(0.3*220.95=66.285)]=275.192g

Ag_2O=115.87*5/275.192=2.1052+(3% extra=0.0631)=2.1683g

Nb_2O_5=93.037*5/275.192=1.6904g

Ta_2O_5=66.285*5/275.192=1.2043g

X=0.4(40%) $Ag(Nb_{0.6}Ta_{0.4})O_3$

Total amount=[115.87+(0.6*132.91=79.746)+(0.4*220.95=88.38)]=283.996g

Ag_2O=115.87*5/283.996=2.0399+(3% extra=0.0611)=2.1010g

Nb_2O_5=79.746*5/283.996=1.4039g

Ta_2O_5=88.38*5/283.996=1.5560g

2.M=Sb(Antimony)

For antimony we take Sb_2O_5 instead of Ta_2O_5 and here we prepare sample 4g for 10%.

Molecular wg.of Sb_2O_5=323.50 $gmol^{-1}$and per atom=323.50/2=161.75$gmol^{-1}$

3.M=V(Vanadium)

Here we take V_2O_5 and make sample 10g for 10%.

Molecular wg. Of V_2O_5=181.88g mol^{-1} and per atom=181.88/2=90.94g mol^{-1}

Syenthesis of $AgNbO_3$ and its constituants after doping.

Solid state route method is one of the best to prepare the sample.The precursors taken are Ag_2O and Nb_2O_5.The different syenthesis techniques that have been done here

- Proper mixing of precursors(Grinding)
- Calcination of powder
- Pallet formation
- Sintering

Now we follow all above mention process one by one

Grinding:For the preparation of $AgNbO_3$ the constituants(Ag_2O,Nb_2O_5) are weighted in an electronic digital balance and after mixing we grind it by using an morter and pastle for 2 hrs.

Calcination:It is a thermal process in which the well grinded mixed precursors are subjected to a suitable tempreture for a well calculated duration for the formation of desired phase.This process is done to remove the volatile element.The present sample Ta,Sb(10%) is calcined at 830^{0c} for 6 hrs. both.

Pallet formation:Thecalcined powder supposed to be characterized by different technique are required to take a proper shape according to the need.The PVA(Polyvinayl alcohol) act as a

binder and then pallet are made by the help of palletizer by applying a pressure nearly 5.5ton.After that sintering is done.

Sintering:It is a high tempreture thermal treatment for densification of ceramic material.Pallet always subjected below its melting point.The present sample is sintered at 1030^{0c} for 3 hrs.

Characterization techniques

There are many characterization techniques but we include here only three which are

- X ray diffraction(XRD)
- Scanning electron microscope(SEM)
- Field emission scanning electron microscopy(FESEM)
- Dielectric study

Now we discus these one by one

XRD: To determine the phase composition of a material we done XRD.X ray crystallography is a technique used for identifying the atomic and molecular structure of a crystal,in which the atom cause a beam of incident x ray to diffract into many specific dirction.From XRD data some other information like mean position of the atom in the crystal,chemical bond etc.can also be get.Some XRD pattern shown below.

SEM:To extract the structural information we do SEM analysis.In SEM we do surface morphology study or we can say that the fundamental of SEM is to study the surface or near surface structure of bulk specimen.SEM is a powerful technique to characterize a specimen of the order of nm or μmscale.SEM image of $AgNbO_3$ in pure form as well as after doping are shown below.

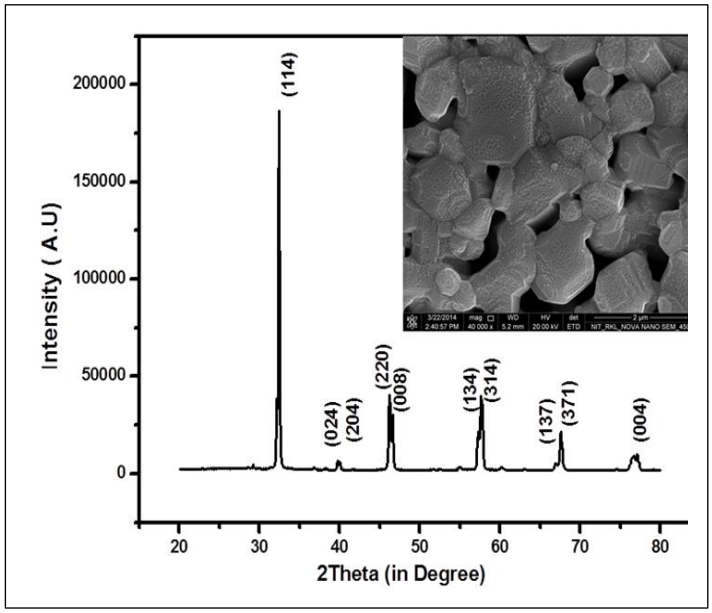
FESEM: It is a characterization technique which is used for highest magnification as far as possible.So from FESEM we can produce clear and less distorted images.This characterization technique is used in physics,chemistry,biology to observe structure that may be as small as 1nm.

ImpedenceAnalyser:For measuring the electric transport properties.The dielectric properties of a substance such as dielectric constant, dielectric loss, relaxation time, modulus, impedance etc. have provided an insight to the structure of the molecules of the system.Dielectric study of $AgNbO_3$(experimental)shown below.

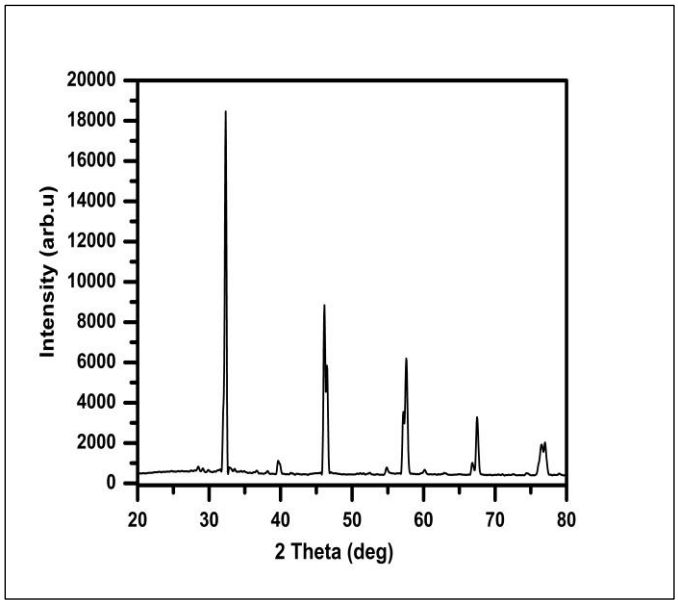
CHAPTER 4

Result and discussion:

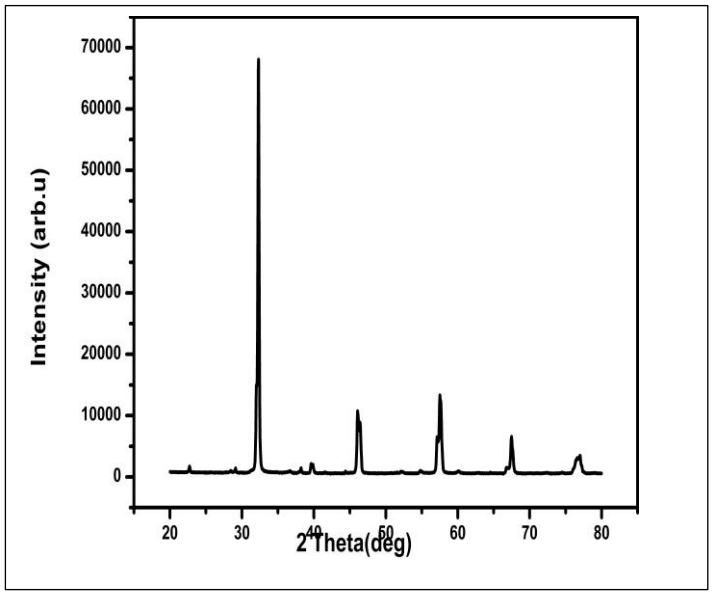
XRD analysis



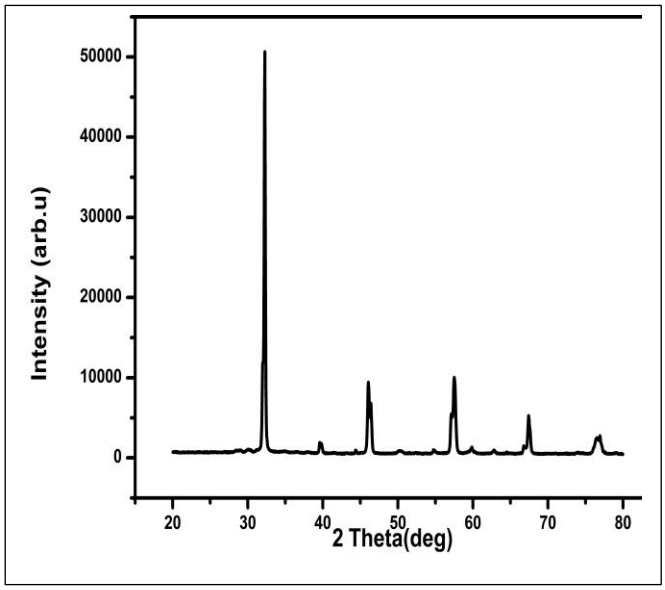
Parent AgNbO3



Vanadium 10 %



Ta 10 %



Sb 10 %

Fig.7

The XRD patterns of all prepared samples are shown in above fig.Positions of all the diffraction peaks match and well indexed to orthorhombic $AgNbO_3$ (JCPDS Card No. 070-4738). Minute traces of secondary phases are unavoidable irrespective of synthesis conditions.XRD pattern are shown in **fig 7**

SEM analysis: For Ta 10% are shown in fig 8

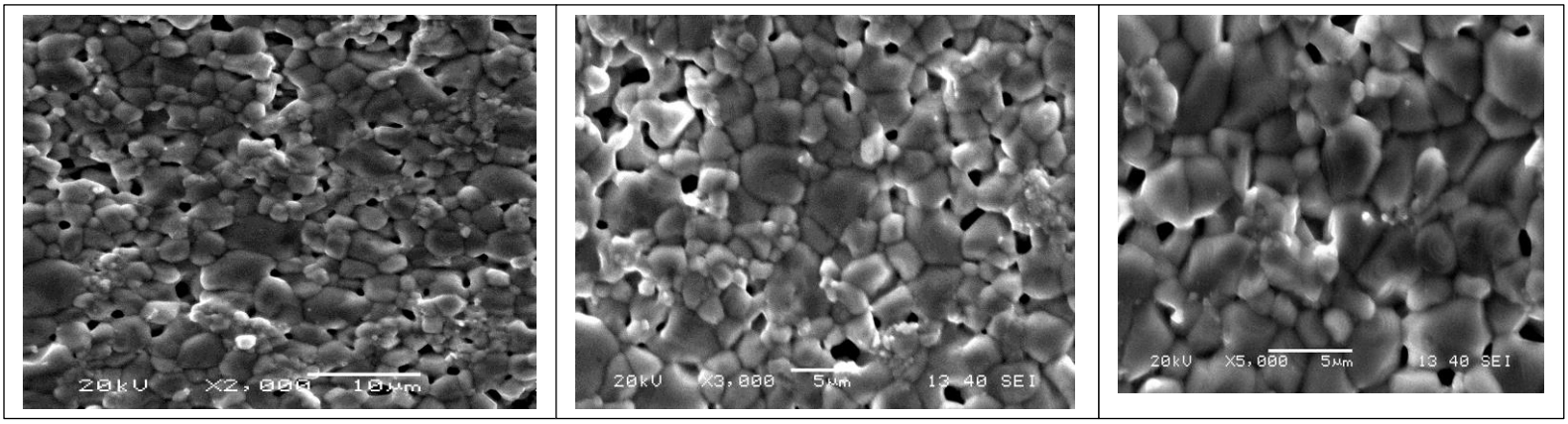


Fig.8

For Sb 10% are shown in fig 9

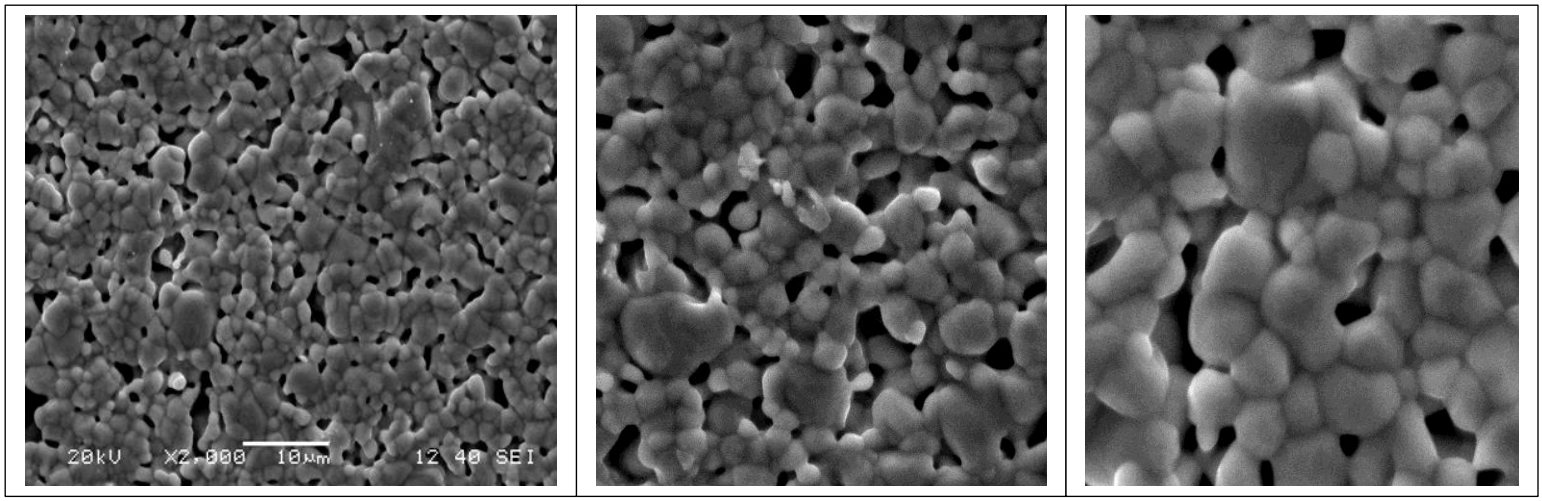
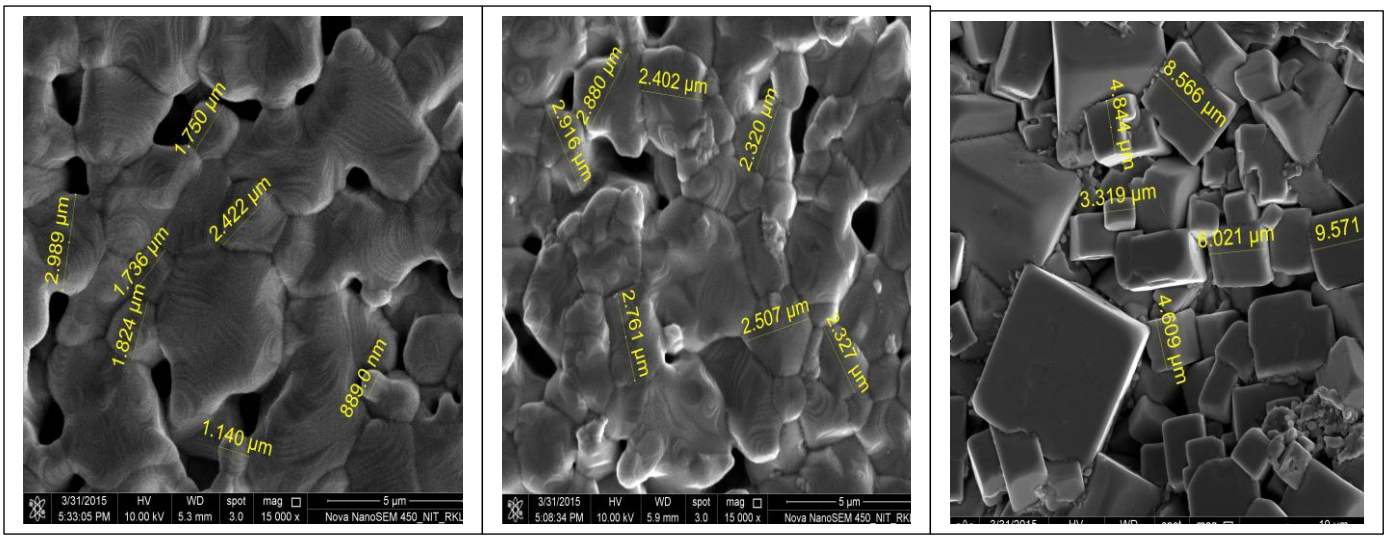


Fig 9

FESEM analysis:

The FESEM image of AN(silver niobate) sample shows distribution of both larger grain size of 5 µm to smaller grain size of 1.2 µm. similar distributions are observed in both ATN and ASN systems with difference of larger and smaller grains reduces in the later cases.No remarkable change in shape of grain is also noticed in the above cases.But in AVN system,the shape of grain changes drastically from polyhedron to brick like structure.Significant increase in grain size is visible though very minute grains also appear in the surface.Presence of pores also observed in all the samples.FESEM image are shown in **fig.10**



Sb 10% **Ta 10%** **V 10%**

Dielectric study:

(a) In dielectric study we show how the dielectric constant and tangent loss very with tempreture and at different frequency(1kHz-5MHz)

(b) In pure $AgNbO_3$(AN system) we see that dielectric constant decrease from 1kHz-1MHz.**(fig.14)**

(c) We have also note down the multiple phase transition at all the frequency.

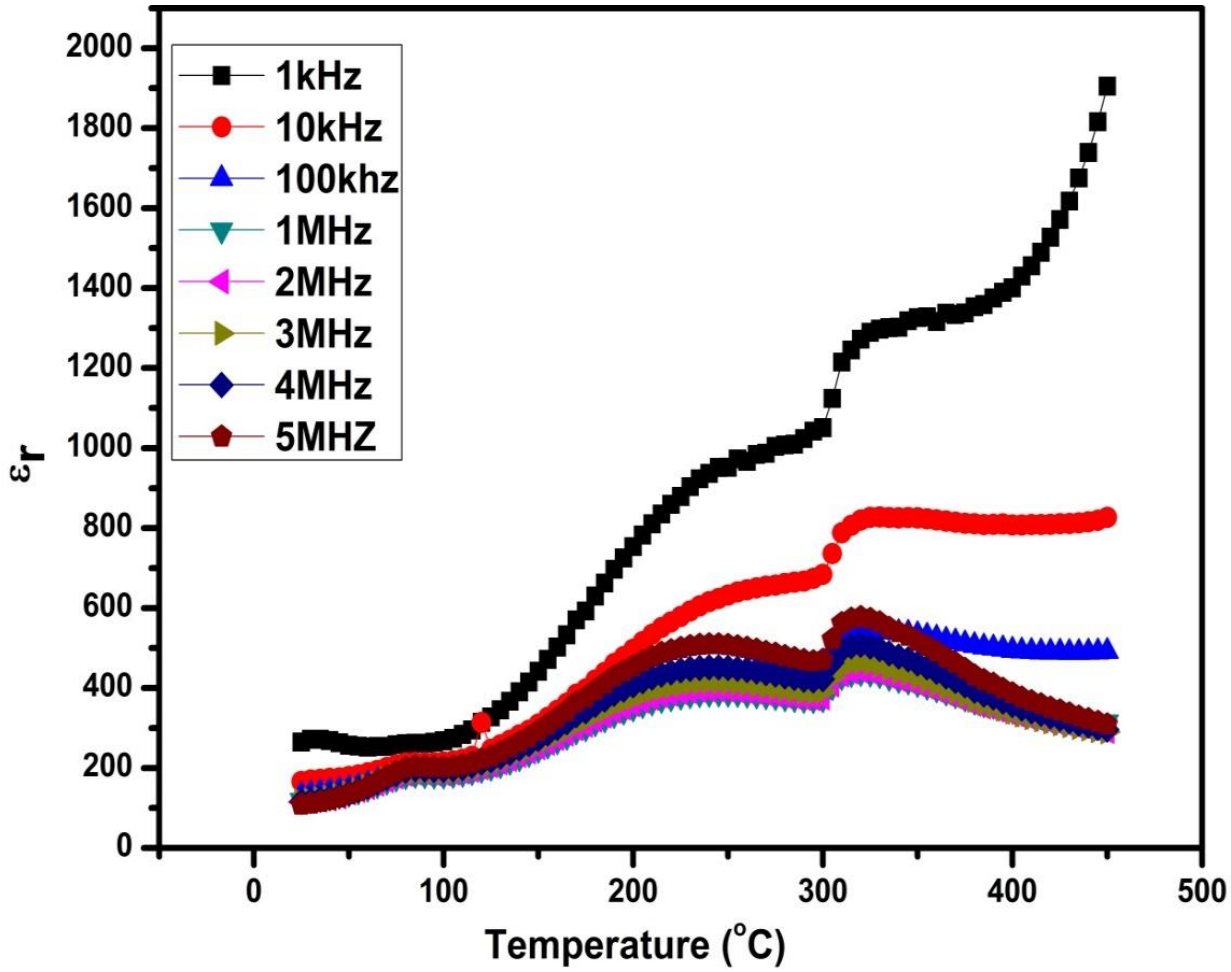
(d) Dielectric constant then increase from 1MHz-5MHz this is exceptional in this material(parent phase of silver niobate)**[fig 15]** but w.r.t. tempreture dielectric decrease after a certain tempreture(Curie tempreture) because when we increase the tempreture there is random orientation of dipole and net dipole moment decrease so polarization decrease and corresponding dielectric constant decrease.

(e) Dielectric loss gradually decrease from 1kHz-1MHz and then increase from 1MHz-5MHz. in the present sample which are shown in **fig.12** and **fig 13.**

(f) **Dielectric** constant data are shown in table below.

Dielectric constant at 10 kHz	AN(Parent)	ATN	ASN	AVN
Tempreture at AFE to PARA	853.77(360^{0C})	645.239(355^{oC})		1527.57(345^{0C})
Tempreture at FE to AFE	330.63(90^{0C})	310(80^{0C})		354.729(75^{0C})
At room tempreture 30^{0C}	171.58	219	600	265.72

Dielectric constant vs tempreture of parent system($AgNbO_3$) at different frequencies are shown in **fig.11**



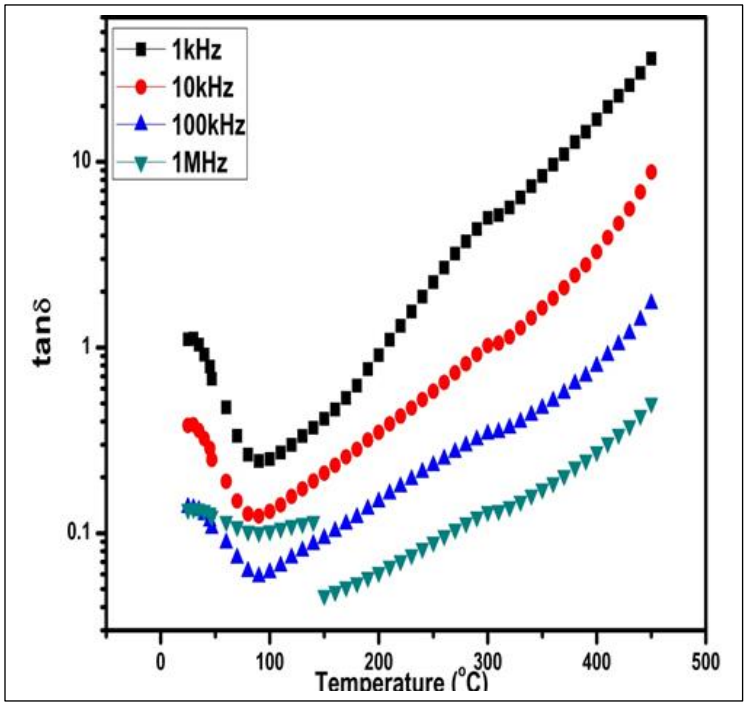


Fig 12

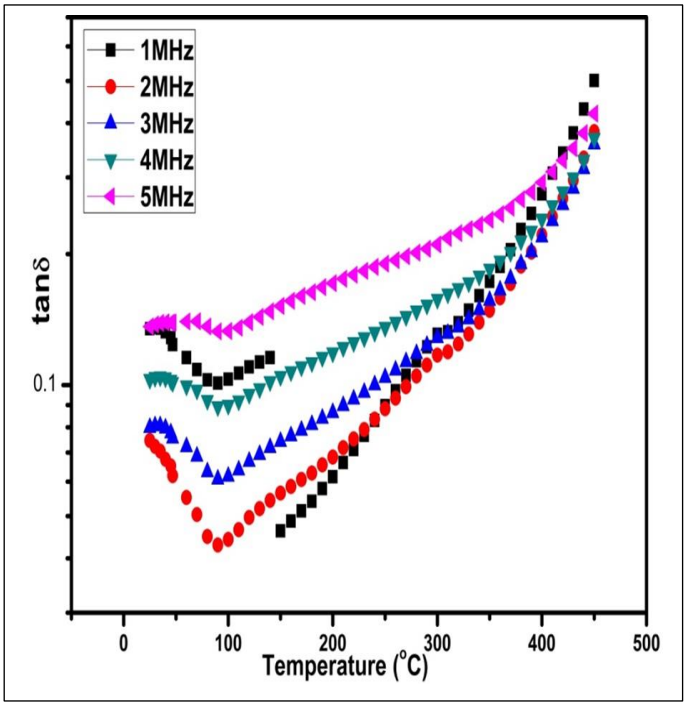


Fig 13

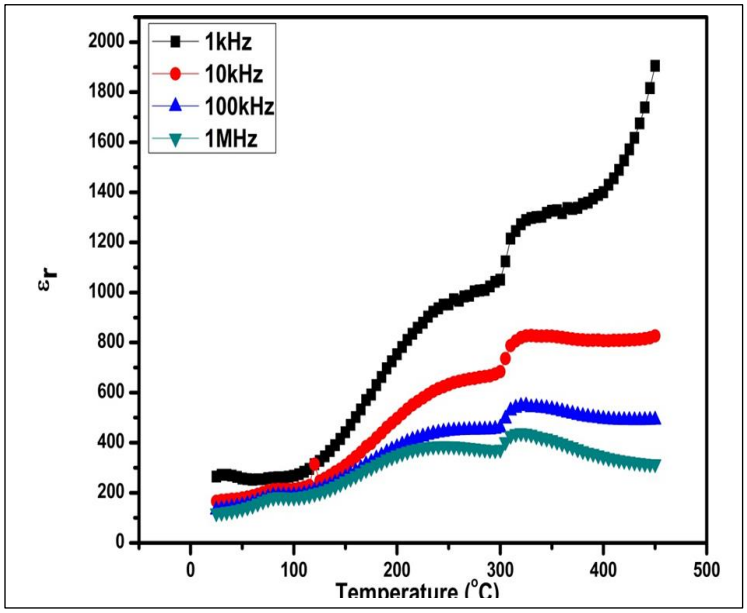


Fig 14

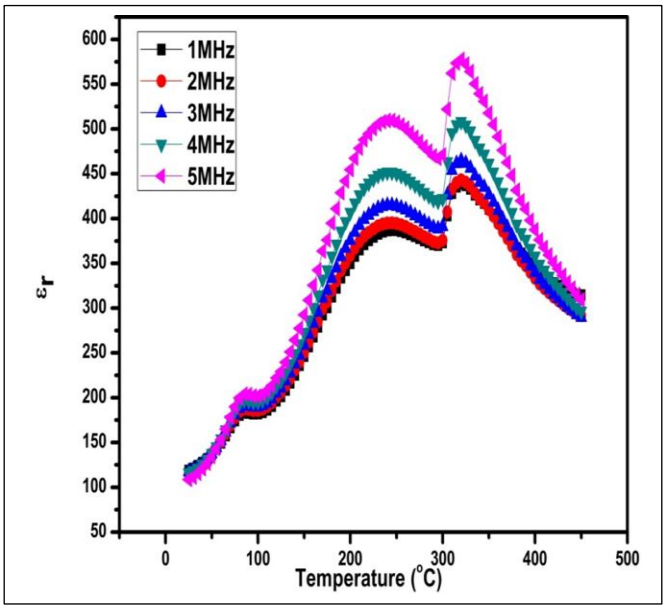


Fig 15

Ferroelectric study:

(g) In ferroelectric study we discus about P-E loop data.All the sample shows P-E hysteresis loop at room tempreture.Applied field and measured polarization value are shown in table below

Applied field	Saturation & remnant polarization($\mu C/cm^2$)	AN	ATN	ASN	AVN
10kV	P_s	0.24	0.36	0.68	0.57
	P_r	0.03	0.06	0.09	0.28
20kV	P_s	0.44	0.67	0.69	0.14
	P_r	0.06	0.11	0.51	0.60

Coresponding to above value P-E loop obtained which I already show in my ppt.

Discussion about dielectric and ferroelectric study:

The enhanced dielectric and ferroelectric fig indicates that polarization must have increased.Increased polarization implies formation of new dipoles or increase in dipole moments.The overall result is due to the net interaction of existing dipole moments.Thoughporosity,density,defect etc. have some adverse effect on the electrical properties still presence of pores in all the sample has been taken of equal contribution.We certainly point out the lattice distortion due to dopants of smaller size are the crucial one in generating new dipoles or increasing the separation between cationic and anionic centres.Vanadium being the smaller ionic radius has larger impact on disturbing the cation and anion center to enhance the dipole moment.

CHAPTER 5

CONCLUSION:

We prepared the $AgNbO_3$(AN) system and its modified by mixed oxide route.Good quality of crystal formation was confirmed by XRD and FESEM analysis. Electric characterization were carried out and observed that modification had brought enhanced dielectric constant. We certainly point out the lattice distortion due to dopants of smaller size are the crucial one in generating new dipoles or increasing the separation between cationic and anionic centers. We have carried out the electric transport properties study of silver niobate ($AgNbO_3$) and its modified by the help of complex impedence and modulus technique. P-E loop study shows that the enhanced ferroelectric properties which indicates that polarization must have increased. So, increased polarization implies the formation of new dipoles which increase in dipole moments. The overall result is due to the net interaction of dipole moments.

REFERENCE:

1. "Dielectrics (physics)". *Britannica*. 2009. p. 1. Retrieved2009-08-12
2. Raymond A. Serway, John W. Jewett, Jr. (2009). *Physics for Scientists and Engineers, Volume 2* (8th ed.). Cengage Learning. p. 756.ISBN 1439048398.
3. A. Navrotsky (1998). "Energetics and Crystal Chemical Systematics among Ilmenite, Lithium Niobate, and Perovskite Structures". *Chem. Mater.*10 (10): 2787. doi:10.1021/cm9801901
4. Wenk, Hans-Rudolf; Bulakh, Andrei (2004). *Minerals: Their Constitution and Origin*. New York, NY: Cambridge University Press. ISBN 978-0-521-52958-7.
5. http://www.process-heating.com/articles/89334-high-temperature-processing-with-calciners
6. "Sinter, v." *Oxford English Dictionary* Second Edition on CD-ROM (v. 4.0) © Oxford University Press 2009
7. Kepler J (1611). *Strena seu de Nive Sexangula*. Frankfurt: G. Tampach. ISBN 3-321-00021-0.
8. Jump up^ Steno N (1669). *De solido intra solidum naturaliter contento dissertationis prodromus*. Florentiae.
9. McMullan, D. (2006). "Scanning electron microscopy 1928–1965". *Scanning* 17 (3): 175. doi:10.1002/sca.4950170309.
10. Joseph Goldstein et. al., *Scanning Electron Microscopy and X-ray microanalysis*, Kluwer Academic/Plenum Publishers, New York , 2003